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New transitions and energy levels of water vapor by high sensitivity CRDS near 1.73 and 1.54 µm

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ABSTRACT

This contribution is part of a long term project aiming at improving the water absorption spectroscopy by high sensitivity cavity ring down spectroscopy (CRDS) in the near infrared.

Two new sources of CRDS spectra are considered:

(i) The room temperature absorption spectrum of water vapor in natural isotopic abundance is recorded near 1.73 µm. A series of recordings was performed from 5693 to 5991 cm^{-1} with a pressure value of about 6 Torr. The noise equivalent absorption (α_{min}) of the spectra is better than 10^{-10} cm^{-1}. A total of 1453 lines were assigned to 1573 transitions of four water isotopologues ($H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$ and $HD^{16}O$). Their intensities span more than five orders of magnitude from 3.0×10^{-30} to 4.7×10^{-25} cm/molecule at 296 K. The assignments were performed using known experimental energy levels as well as calculated line lists based on the results of Schwenke and Partridge.

Two hundred fifty-one lines (assigned to 280 transitions) are observed for the first time and twelve energy levels are newly determined. The comparison of the obtained line parameters with those of the HITRAN database is discussed. Forty-six line positions are observed to significantly differ from their HITRAN values ($\delta\nu = \left|\nu^{HITRAN} - \nu^{CRDS}\right| > 0.02$ cm^{-1}). The derived set of energy levels is compared to those recommended by an IUPAC task group.

(ii) The room temperature CRDS spectrum of water vapor highly enriched in ^{17}O was recorded near 1.54 µm (6223–6672 cm^{-1}) at a pressure of 12 Torr. Compared to a previous study, the higher pressure of the recordings allowed for extending the observations. Overall, twenty-six new levels were determined for both $H_2{}^{17}O$ and $HD^{17}O$.

All these observations together with other recent measurements will allow for an extension and an update of our empirical database in the 5693– 8340 cm^{-1} region.

1. Introduction

The present work is a continuation of previous studies devoted to an extensive investigation of the near infrared water vapor absorption spectrum by highly sensitive cavity ring down spectroscopy (CRDS) [1–6]. From these investigations, we have constructed an empirical spectroscopic database for water vapor in the 5850–8340 cm^{-1} region [7] which is reproduced in the GEISA database [8] and constitutes the main source of water line positions used in the current version of the HITRAN database [9] in the region.

In the present contribution we extend the CRDS recordings to lower wavenumbers, down to 5693 cm^{-1}. As illustrated in Fig. 1, the investigated region corresponds to the low energy edge of the 1.6 µm atmospheric window mainly formed by transitions to the second triad (cold bands) and first hexad (hot bands). Some lines near 5700 cm^{-1} are very strong (line intensity up to 10^{-22} cm/molecule) and not suitable for measurements by CRDS. Consequently, new observations are mostly limited to spectral intervals between the strong lines. The most sensitive previous study in the region is due to Jenouvrier et al. which reported lines with intensity as small as 5×10^{-27} cm/molecule by Fourier transform spectroscopy (FTS) using an absorption path length up to 1.8 km [10]. Above 5851 cm^{-1}, our previous CRDS study lowered the detection threshold down to 10^{-29} cm/molecule [5]. The newly

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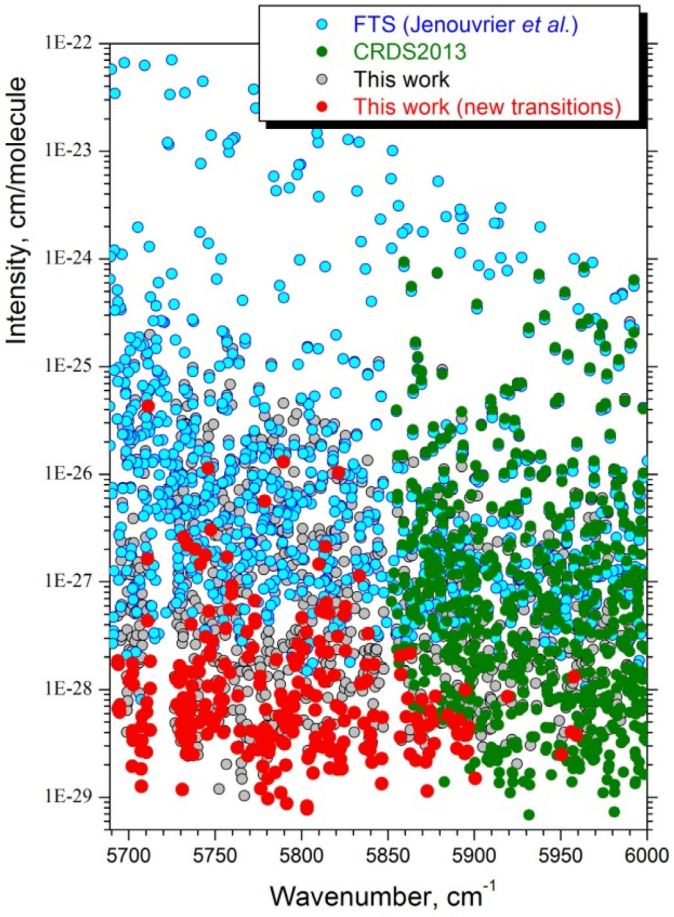

Fig. 1. Overview of different line lists of water vapor in the investigated region (5693–5991 cm^{-1}) obtained by FTS with long absorption path length (blue dots) [10], by CRDS above 5851 cm^{-1} (green dots) [5] and in this work (red dots for the newly detected lines, grey dots otherwise).

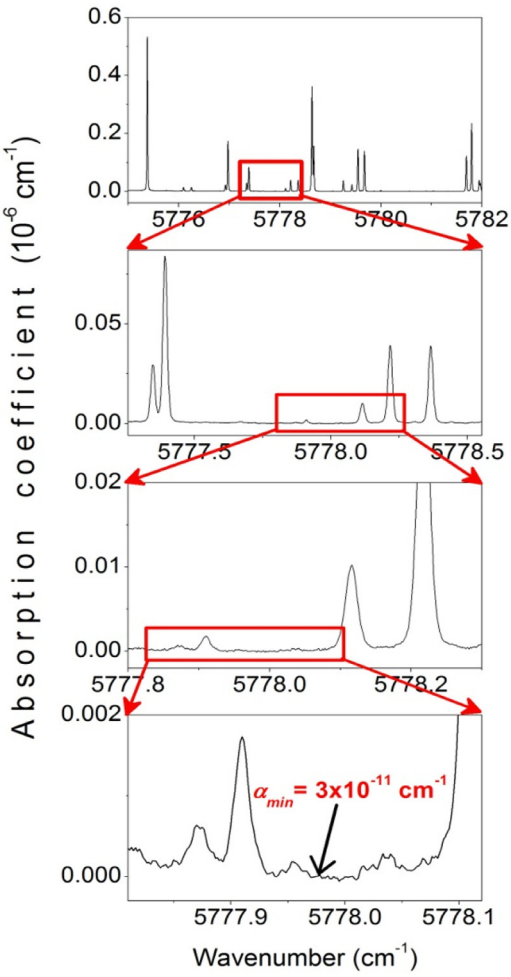

Fig. 2. CRDS spectrum of natural water vapor near 5778 cm^{-1}. The sample pressure was 5.65 Torr. The successive enlargements illustrate the high dynamics of the recordings and the noise level on the order of $\alpha_{min} \sim 3 \times 10^{-11}$ cm^{-1}.

recorded spectra cover the 5693–5991 cm^{-1} interval. As expected, most of the new observations (highlighted on Fig. 1) concern the 5693–5851 cm^{-1} region, newly investigated by CRDS.

In the last years we have devoted specific efforts to the $H_2{}^{17}O$ minor isotopologue [11–14] (3.72×10^{-4} relative natural abundance [9]) for which the knowledge of the near infrared spectrum was particularly scarce. For instance, very recently, we determined about one hundred new energy levels, mostly of $H_2{}^{17}O$ and $HD^{17}O$, from a CRDS study performed with water vapor highly enriched in ^{17}O in the same spectral region considered in the present study for natural water [14]. We take the opportunity of the present contribution to report on new observations relative to the ^{17}O isotopologues in the 6223–6672 cm^{-1} region, already investigated in Ref. [11] from CRDS spectra of water vapor highly enriched in ^{17}O recorded at about 1 Torr. Here, the analyzed CRDS spectra were recorded at a pressure of 12 Torr. The higher pressure of the recordings allowed a total of 52 levels of $H_2{}^{17}O$ and $HD^{17}O$ to be newly determined.

In the next paragraph, the CRDS recordings performed with natural water are described together with the retrieval of the spectroscopic parameters and the construction of the line list. The rovibrational analysis is presented in Section 3 which includes the comparison to literature in particular to the present version of the water vapor list in the HITRAN database [7] and to the energy levels recommended by an IUPAC task group (IUPAC-TG hereafter) [15–17]. The results relative to the analysis of the ^{17}O isotopologues near 6500 cm^{-1} are presented in Section 4 before the concluding remarks (Section 5).

2. Experimental set up

The description of the CRD spectrometer has been presented in Refs. [1,18]. In the present work, thirteen fibered Distributed Feedback (DFB) laser diodes were used as light sources. The typical tuning range of each laser diode was about 25 cm^{-1} by temperature variation from −5 °C to 55 °C allowing the coverage of the 5693–5991 cm^{-1} range except for a few spectral gaps: 5712.9–5722.1, 5742.1–5744.1, 5774.1–5774.9, 5847.6–5854.3 cm^{-1}. The finesse of the cavity varied from 130,000 at 5850 cm^{-1} to 200,000 at 5700 cm^{-1} resulting in measured ring down (RD) times from 200 µs to 300 µs, respectively. About 30–100 RD events were averaged per spectral point leading to a minimum detectable absorption coefficient (evaluated as the *rms* of the baseline fluctuation), α_{min}, between 1×10^{-10} cm^{-1} and 2×10^{-11} cm^{-1} depending on the RD time. The sensitivity and high dynamics of the recordings are illustrated on Fig. 2.

The cell temperature was measured with a temperature sensor (TSic 501, IST-AG, 0.1 K accuracy) fixed on the cell surface, covered by an external blanket of foam for thermal isolation. During the measurement campaign, the cell temperature varied between 295.20 and 297.14 K. The frequency calibration of the spectra relies on the frequency values provided by a commercial wavelength me-

ter (Bristol 621A, ±10 MHz repeatability over 5 min, ±34 MHz accuracy at 5700 cm^{-1}). This calibration was then refined using accurate water line positions provided by the HITRAN2016 database [9]. The uncertainty on the line center is estimated to be 1×10^{-3} cm^{-1} for unblended. A larger error bar on the order of 0.002 cm^{-1} is probably a reasonable estimate in the case of the weak lines considered in this work.

At the beginning of each recording, the water sample was purified by cooling with liquid nitrogen and pumping on the residual vapor phase. During the recordings, performed in static regime, the gas pressure was continuously measured by a capacitance gauge (MKS Baratron, 10 Torr, 0.15% accuracy of the reading). The average pressure value was about 6 Torr but the pressure was observed to vary during the spectra recordings (typically 2 hours for each DFB laser diode). This is due to the adsorption of water molecules on the walls of the CRDS cell after a long pumping period (and to the high surface/volume ratio of the cell). A pressure decrease up to 1 Torr was observed during some recordings. Consequently, in the derivation of the line intensities the exact pressure value at the time of the recording of the considered line was used.

The line parameters were obtained by using a homemade interactive least squares multi-lines fitting program written in LabVIEW. A Voigt profile with the width of the Gaussian component fixed to the calculated Doppler broadening was adopted for each line. The global line list provided as Supplementary Material gathers line parameters retrieved from the different recordings. It counts a total of about 2100 lines whose assignment is discussed in the next paragraph.

3. Spectrum analysis and comparison to literature

3.1. Rovibrational assignments

Among the 2064 absorption lines of the global list, 1453 lines were assigned to 1573 transitions of the four most abundant water isotopologues ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$ and $HD^{16}O$). The assignments were performed using known experimental energy levels [11,13–17,31] as well as calculated line lists based on the results of Schwenke and Partridge [19–21]. Previous studies in the region were reported in Refs. [2,5,10,22–25] for natural water vapor and in Refs. [26–29], Refs. [11,14] and Refs. [30,31] for samples highly enriched in ^{18}O, ^{17}O and D, respectively. Most of the overall set of measurements (about 2500 lines in total) were obtained from CRDS studies [2,5,11,14,29,31].

Among the water lines, 251 lines (assigned to 280 transitions) are observed for the first time (191, 3, 7 and 50 for $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$ and $HD^{16}O$, respectively). Most of the new lines have intensity smaller than 5×10^{-28} cm/molecule and are located below 5850 cm^{-1} (see Fig. 1). New lines of $H_2{}^{16}O$, $H_2{}^{17}O$ and $HD^{16}O$ allowed the determination of twelve new upper energy levels with corresponding term values listed in Table 1**.** Their error bar is estimated to be around 0.002 cm^{-1}.

A large part of the 610 remaining lines was identified as due to impurities present in the water sample: methane (52 lines), formaldehyde (150 lines) and ammonia (214 lines). Lines due to CH_4, H_2CO and NH_3 were identified by comparison to the HITRAN database [9], Ref. [32] and a FTS spectrum (with reference 910606R016) in open access at the Kitt Peak data center, respectively. Lines of formaldehyde which is probably desorbing from the set up were identified in the low energy part of the spectrum below 5850 cm^{-1}. As no data are provided by the HITRAN database in the studied region, the CH_2O lines were identified by comparison with the FTS spectrum of Ref. [32].

All the impurity lines found in our list have intensity (including the abundance factor) less than 10^{-27} cm/molecule. Estimated values of the relative abundances of CH_4, H_2CO and NH_3, are 0.1 ppm, 10 and 5 ppm, respectively. One hundred ninety-four weak lines, probably due to unidentified impurities, were left unassigned (intensity smaller than 3×10^{-28} cm/molecule).

Table 1
Term values of $H_2{}^{16}O$, $H_2{}^{17}O$ and $HD^{16}O$ levels newly determined from the CRDS water vapor spectrum between 5693 and 5991 cm^{-1}.

$\nu_1\nu_2\nu_3$	J	K_a	K_c	Term value (cm^{-1})
$H_2{}^{16}O$				
050	1	1	1	7622.6470
$H_2{}^{17}O$				
110	11	3	9	6922.5500
$HD^{16}O$				
040	4	4	1	5943.4355
040	4	4	0	5943.4338
040	6	3	3	5972.4165
040	12	2	10	6882.3271
040	14	1	13	7139.9806
040	14	2	13	7143.1366
040	14	2	12	7313.5033
120	9	5	5	6652.0999
120	11	6	6	7171.1371
120	12	3	9	6901.5553

3.2. Comparison to the HITRAN database and to the IUPAC-TG energy levels

The HITRAN line list [9] contains 2625 transitions of the four most abundant water isotopologues between 5693 and 5991 cm^{-1}. Among the 1051 $H_2{}^{16}O$ transitions assigned in our spectrum, 67 transitions (maximum intensity of 4.4×10^{-28} cm/molecule) are missing in the HITRAN list. Twenty of them have intensity below the HITRAN cut-off (10^{-29} cm/molecule). Among the other missing transitions, 29 belong to the $3\nu_2$, $4\nu_2$ and $5\nu_2-\nu_2$ pure bending bands and 15 are transitions with high ΔK_a value of the $\nu_1+\nu_2$ and $\nu_2+\nu_3$ bands. The absence of these weak transitions in the HITRAN database might be related to the variational origin of the HITRAN line intensities. Most of the HITRAN intensities in the region have been computed by variational calculations based on an empirically adjusted potential energy surface (PES) and an *ab initio* dipole moment surface (DMS) [33–36]. In general, variational intensities are known to be accurate but this is not the case for purely bending bands or in case of local resonance interactions (the high ΔK_a lines are observed through an intensity transfer induced by a local resonance interaction). In some cases, variational intensities are calculated significantly smaller than measured. Part of the missing lines may have their variational intensities underestimated and thus below the HITRAN intensity cut-off.

Conversely, we show on Fig. 3 an example where a $4\nu_2$ transition of $H_2{}^{16}O$ is given in the HITRAN database with a strongly overestimated intensity. The $4\nu_2$ $12_{4\ 9}$–$13_{5\ 8}$ line at 5940.796 cm^{-1} is not observed by CRDS while it has a 5.487×10^{-27} cm/molecule HITRAN intensity due to Toth [37] (the line position was calculated from the IUPAC-TG energy levels [17]). Note that the variational intensity calculated by Schwenke and Partridge (5.5×10^{-30} cm/molecule) [20,21] is 3 orders of magnitude smaller than HITRAN value.

As concerned line positions, the overall agreement between CRDS and HITRAN values is satisfactory. Nevertheless, as illustrated in Fig. 4, differences $\delta\nu = |\nu^{HITRAN} - \nu^{CRDS}|$ larger than 0.015 cm^{-1} are noted for four lines, with a maximum value of 0.257 cm^{-1} for the $\nu_2+\nu_3$ $18_{7\ 12}$–$17_{7\ 11}$ line position at 5776.0016 cm^{-1}. Their HITRAN positions were derived from inaccurate empirical energy levels.

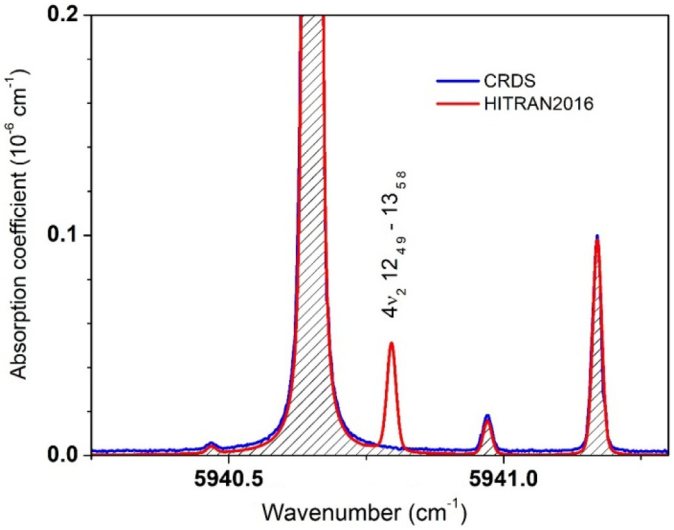

Fig. 3. Comparison of the CRDS spectrum (blue line) to a simulation performed using the HITRAN line list [9] (red line). The pressure of water vapor in natural isotopic abundance is 6.26 Torr. The HITRAN intensity of the $4\nu_2\ 12_{4\,9} - 13_{5\,8}$ line of $H_2{}^{16}O$ from Toth [37] is strongly overestimated.

Among the 523 transitions assigned to $H_2{}^{18}O$, $H_2{}^{17}O$ and $HD^{16}O$, 57 are not included in the HITRAN line list because their intensity is below the HITRAN intensity cut-off. The largest position discrepancies concern the $\nu_1+\nu_2$ and $\nu_2+\nu_3$ bands of $H_2{}^{17}O$ ($\delta\nu_{max} = 0.086$ cm^{-1} for $\nu_1+\nu_2\ 8_{5\,4}$–$7_{2\,5}$) at 5739.09622 cm^{-1}) and $H_2{}^{18}O$ ($\delta\nu_{max} = 0.064$ cm^{-1} for $\nu_1+\nu_2\ 13_{4\,9}$–$12_{3\,10}$ at 5801.30686 cm^{-1}) and the $4\nu_2$ band of $HD^{16}O$ ($\delta\nu_{max} = 0.1012$ cm^{-1} for the $4\nu_2\ 14_{2\,12}$–$13_{2\,11}$ transition at 5780.77138 cm^{-1}).

In summary, our recordings will help to correct a number of inaccuracies in the present version of the HITRAN list and to complete it with at least 47 $H_2{}^{16}O$ transitions and one $H_2{}^{17}O$ transition with intensity above the HITRAN cut-off.

We have performed a systematic comparison of the upper energy levels derived from the present CRDS recordings to those recommended by the IUPAC-TG [15–17]. Among the 1051 $H_2{}^{16}O$ transitions assigned in our spectra, all but one ($5\nu_2$–$\nu_2\ 1_{1\,1}$–$2_{0\,2}$ at 5957.68242 cm^{-1}) can be calculated from IUPAC-TG empirical energy levels [17]. The differences are all within 0.018 cm^{-1}.

Among the 189 $H_2{}^{17}O$ transitions, 64 reach an upper energy level missing in the IUPAC-TG dataset [15] (mainly for the (030), (011) and (110) states of the second triad). The largest differences concern the $\nu_1+\nu_2$ and $\nu_2+\nu_3$ bands (maximum deviation of 0.048 cm^{-1} for the $\nu_1+\nu_2\ 8_{5\,3}$–$7_{2\,6}$ line position).

Only eight transitions of the $\nu_1+\nu_2$ $H_2{}^{18}O$ band cannot be calculated using the IUPAC-TG energy levels [15]. Other 196 calculated positions are in good agreement with our CRDS values. All but one differences are within 0.01 cm^{-1}. The $\nu_2+\nu_3\ 7_{6\,1}$–$6_{2\,5}$ line position shows the largest deviation (0.025 cm^{-1}).

Forty-one $HD^{16}O$ transitions of the $4\nu_2$, $\nu_1+2\nu_3$ and $\nu_1+\nu_3$ bands reach upper energy levels absent in the corresponding IUPAC-TG dataset [16]. All but two position differences are within 0.014 cm^{-1}. The two largest deviations concern transitions of the $4\nu_2$ band: $10_{4\,7}$–$9_{4\,6}$ line at 5798.15917 cm^{-1}($\delta\nu = 0.061$ cm^{-1}) and $10_{4\,6}$–$9_{4\,5}$ line at 5798.26085 cm^{-1}($\delta\nu = 0.067$ cm^{-1}).

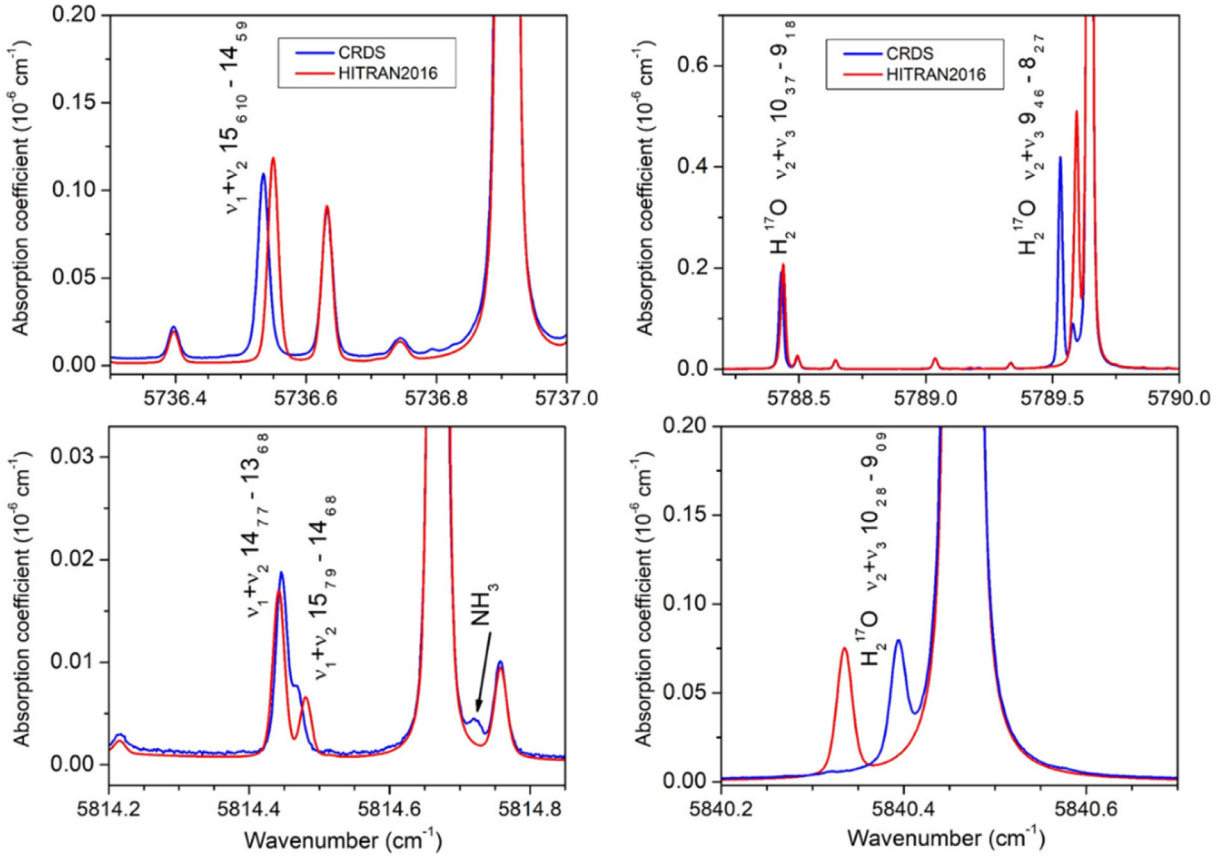

Fig. 4. Comparison of the CRDS spectrum (blue line) to a simulation performed using the HITRAN line list [9] (red line) for water in natural isotopic abundance. The pressure of water vapor was about 6 Torr.
Left panels: Inaccurate HITRAN positions of lines of the $\nu_1+\nu_2$ band of $H_2{}^{16}O$,
Right panels: Inaccurate HITRAN positions of lines of the $\nu_2+\nu_3$ band of $H_2{}^{17}O$ (in natural isotopic abundance).

4. CRDS spectrum of ^{17}O highly enriched water vapor between 6223 and 6672 cm^{-1}

In Ref. [11], we reported on the study of the absorption spectrum of water vapor highly enriched in ^{17}O between 5850 and 6671 cm^{-1}. This spectral region corresponds to a transparency window of the water molecule (see Fig. 5) which was poorly characterized for ^{17}O isotopologues. More than 1000 energy levels of $H_2{}^{17}O$ and $HD^{17}O$ were newly determined in Ref. [11]. The analysis relied on recordings at 12.0 and 1.0 Torr for the spectral region below and above 6223 cm^{-1}, respectively. We take the opportunity of the present contribution to report some additional results obtained by considering the spectra recorded at 12 Torr above 6223 cm^{-1} not considered in Ref. [11]. The higher pressure allowed detecting a number of weak lines and thus the determination of a set of new energy levels of $H_2{}^{17}O$ and $HD^{17}O$. The reader is referred to Ref. [11] for the details about the spectra recordings. Let us recall that estimated values of the relative abundances of the $H_2{}^{17}O$ and $HD^{17}O$ isotopologues in our sample are 62.7% and 0.0126%, respectively [11].

We did not construct a global line list for the 12 Torr spectra but focused on new lines of $H_2{}^{17}O$ and $HD^{17}O$ too weak to be measured at 1 Torr. As illustrated in Fig. 6, these lines are located between the strong absorption lines in the region, some of the latter having intensity larger by more than four orders of magnitude.

Overall, line parameters of 257 lines were obtained by using the same interactive least squares multi-lines fitting program as described above for the analysis of the natural water spectrum. These lines were assigned to 106 and 165 transitions of $H_2{}^{17}O$ and $HD^{17}O$, respectively (see Supplementary Material). Thirty-one of them were observed but not identified in Ref. [11]. Fifty-seven lines were assigned to 60 transitions of $H_2{}^{17}O$ and $HD^{17}O$ associated with new energy levels. These assignments allow obtaining 52 previously unknown energy levels listed in Table 2.

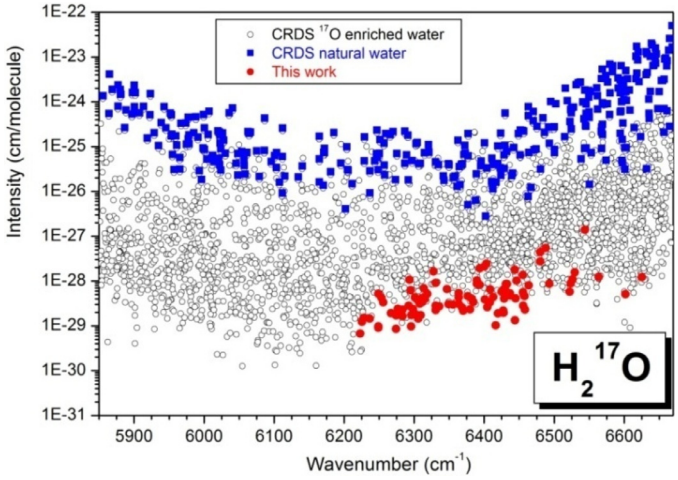

Fig. 5. Available experimental line lists for the $H_2{}^{17}O$ isotopologue in the 5850–6630 cm^{-1} range. Previous observations of $H_2{}^{17}O$ lines in the region were reported from CRDS spectra of natural water [1,2,5] (blue squares) and from Ref. [11] by CRDS of a ^{17}O highly enriched water sample (open circles). The very weak $H_2{}^{17}O$ lines assigned in this work in the 12 Torr spectrum are highlighted (red circles).

It is worth mentioning that the $\nu_2+\nu_3$ $16_{10\,7}$–$15_{8\,8}$ transition at 6223.0418 cm^{-1} allows the first determination of the $15_{8\,8}$ rotational energy level in the vibrational ground state. The energy of the (011) $16_{10\,7}$ upper level (10035.8957 cm^{-1}) was determined in Ref. [11] from the line position of the $\nu_2+\nu_3$ $16_{10\,7}$–$15_{10\,6}$ transition at 5769.46908 cm^{-1}. A value of 3812.8539 cm^{-1} is derived for the (000) $15_{8\,8}$ rotational level in very good agreement with a value (3812.8555 cm^{-1}) calculated using ground state constants [38].

As the empirical value of the $15_{7\,9}$ ground state level is unknown, the term value of the (200) $14_{6\,8}$ upper level

Table 2
Term values of $H_2{}^{17}O$ and $HD^{17}O$ levels newly determined from the spectrum of water vapor enriched in ^{17}O recorded between 6223 and 6672 cm^{-1} at a pressure of about 12 Torr. The estimated error bar is estimated to 0.002 cm^{-1}.

$H_2{}^{17}O$					$HD^{17}O$				
$\nu_1\nu_2\nu_3$	J	K_a	K_c	Term value (cm^{-1})	$\nu_1\nu_2\nu_3$	J	K_a	K_c	Term value (cm^{-1})
000	*15*	*8*	*8*	*3812.8539*[a]	021	10	3	8	7456.7680
021	17	2	16	10127.3159	021	10	4	6	7590.5913
031	12	2	10	10391.1302	021	10	5	5	7738.9162
031	14	0	14	10365.7816	021	10	6	5	7921.6412
040	12	4	8	8570.8779	021	11	3	8	7673.2096
040	15	4	11	9608.6735	021	11	5	6	7911.6773
040	16	1	16	8753.4649	021	11	6	6	8092.3587
040	17	0	17	9068.1282	021	11	6	5	8092.4713
040	18	0	18	9401.8436	021	12	2	10	7787.7044
040	18	1	18	9401.8431	021	13	2	11	7989.2423
050	5	4	2	8586.5033	031	0	0	0	7738.8543
050	10	3	8	9273.3687	031	1	1	1	7773.2642
050	10	4	7	9548.7163	031	2	1	2	7800.7381
110	12	7	5	7901.7601	031	6	0	6	8039.5927
110	14	7	8	8543.2416	031	10	1	10	8486.3341
120	14	2	12	9346.5673	050	12	1	12	7735.7358
120	15	3	13	9661.8632	101	13	5	9	8142.5300
120	17	0	17	9642.7214	101	13	5	8	8148.1653
120	17	1	17	9642.7368	101	14	2	12	8097.7469
130	8	4	5	9535.7165	101	15	4	11	8513.0022
130	9	4	5	9758.8155	111	5	2	3	8057.7927
130	10	1	9	9587.7020	111	5	3	2	8138.2131
200	12	12	1	10741.8477	210	11	3	8	7908.0994
200	12	12	0	10741.8483	210	11	4	7	7997.6054
200	13	10	4	10574.5287	210	12	1	12	7764.9213
200	13	10	3	10574.5296					
200	14	6	8	10178.4870					

[a] Ground state energy level newly determined (see Text).

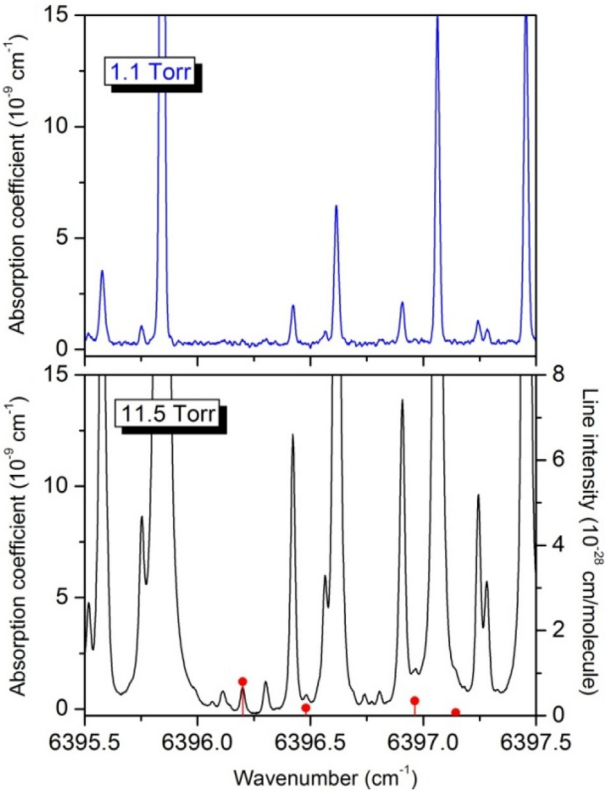

Fig. 6. Comparison of the CRDS spectra recorded at 1.1 Torr (upper panel) and 11.5 Torr (lower panel).
The 1.1 Torr spectrum was analyzed in Ref. [11]. In the present work, the 11.5 Torr spectrum was used to measure weak $H_2{}^{17}O$ and $HD^{17}O$ as those marked with red sticks on the lower panel.

(10178.487 cm^{-1}) was obtained from the line position of the $2\nu_1$ $14_{6\,8}$–$15_{7\,9}$ transition at 6563.6130 cm^{-1} using the $15_{7\,9}$ calculated rotational energy level (3614.874 cm^{-1} [38]).

5. Conclusion

A total of 64 new empirical energy levels have been determined from two CRDS investigations of the near infrared absorption spectrum of water vapor with a natural sample near 1.73 µm and a ^{17}O enriched sample near 1.54 µm. Some inaccuracies in the water list provided by the HITRAN database have been evidenced and discussed both for line positions and line intensities.

The present results together with other measurements obtained by CRDS in the recent years [11–14,39] will allow for an extension and an update of our empirical database in the 5693–8340 cm^{-1} region [7]. In particular the set of empirical energy levels has been significantly extended and the accuracy of the level determinations has been improved in several studies using CRDS referenced to a frequency comb [12,13,39].

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jqsrt.2019.106574.

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